Bi-Layer Single Atom Catalysts Boosted Nitrate-to-Ammonia Electroreduction with High Activity and Selectivity

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ABSTRACT

Designing efficient single atom catalysts (SACs) with high selectivity for electrocatalytic nitrate reduction toward ammonia formation is important but still challenging due to the complex competing electronic interactions between the intermediates, metal active centers, and coordination environments and lack of proper descriptor. Herein, we have reported how to boost the activity and selectivity for electrocatalytic nitrate reduction reaction (NO_3RR) from single layer SACs to bilayer SACs (BSACs) catalysts through axial d-d orbital hybridization based on the systematic investigation of 27 SACs and BSACs using density functional theory (DFT) calculations. Importantly, a two-dimensional volcano relationship between the d-band center (ε_d), dxz+dyz orbital occupation number and the limiting potential (U_L) was developed to describe their NO_3RR catalytic performance. The best BSACs should have simultaneously proper ε_d and dxz+dyz occupation numbers. The BSACs Ti-Mo and Ti-Ta were identified as excellent NO_3RR catalyst candidates with a U_L both at as low as -0.13 V. The hybridization between dz^2-dz^2 orbitals enhanced the charge transfer and structural stability between doublelayer metals. Ultimately, this work shed insight into rational optimizing nitrate reduction on SACs and BSACs, and could guide the design of improved electrocatalysts.